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PROCESS OF CONDITIONING CELLULOSE FIBER FOR CONVERSION INTO CELLULOSE DERIVATIVES, AND PRODUCT OF SAME.

No Drawing.

Application filed October 9, 1926. Serial No. 140,676.

This invention relates to the preparation of nitrocelluloses and has for its object to provide a process of conditioning cellulose material to render it more economical and satisfactory for the preparation of cellulose esters or derivatives and more particularly the lower nitrocelluloses, such as those customarily employed in the manufacture of films, lacquers, artificial silk, and kindred products.

While the process hereinafter described may be practised on various cellulose fibers such as cotton fiber, sulphite fiber, and the like, it may be practised with especial advantage on chemical wood fiber containing a high percentage of alpha or resistant cellulose and which for convenience of designation will hereinafter be termed "alpha fiber." Such fiber may be produced as described in application for patent, Serial No. 75,522, filed December 1, 1925, by George A. Richter and Milton O. Schur, by treating a raw or unbleached pulp—a usual commercial, unbleached sulphite pulp containing 85% to 87% alpha cellulose, for example—with a solution of caustic soda or equivalent alkaline compound, under the proper concentration, temperature and time conditions. During the treatment, an appreciable portion of the non-alpha cellulose constituent of the pulp is dissolved and removed, resulting in a purified or refined fiber which contains upward of 93% alpha cellulose, and which requires only a relatively small amount of bleach for conversion into a fiber of high whiteness and usable as a new rag or cotton fiber substitute, not only in the preparation of cellulose derivatives of high purity and commercial value, but also in the manufacture of bond, ledger and writing papers of the finest quality.

In certain cases, the alkaline treatment may be supplemented by other treating steps. Thus, it may be desirable, especially when the raw pulp contains a percentage of non-alpha cellulose constituent higher than usual, to pretreat the pulp with an oxidizing solution, e. g., a chlorine solution, to remove a portion of such constituent or facilitate subsequent removal with the alkaline treating solution. Or if an alpha fiber of very high

cellulose content, say, 95% to 98%, is desired, the alkaline treatment may be followed by a second alkaline treatment, as described in application for patent, Serial No. 75,888, filed December 16, 1925, by George A. Richter. By a double alkaline treatment, the quantity of bleach necessary to produce a fiber of high whiteness is further reduced. The bleached, refined fiber serves as an excellent raw material for the preparation of cellulose derivatives.

We have discovered that if cellulose fiber, and more particularly an alpha fiber such as hereinbefore described, is rendered less absorptive, the characteristics of such fiber for conversion to cellulose derivatives and more especially nitrocelluloses, are markedly improved. In our application, Serial No. 140,674, filed October 9, 1926, we have described various procedures for decreasing the absorptivity of the fiber, including treatment with suitable filling materials, such as nitrocellulose or regenerated cellulose. This application is a division of the application so identified and covers this particular subject matter.

Our theory is that when pulp is highly absorptive, it is attacked rapidly by the sulphuric acid present in the mixed nitrating acid, partly dissolving or forming unstable esters therewith, which are hydrolyzed and dissolved during subsequent washing of the product, resulting in a low yield and high acid retention. This condition, it is believed, is true to an extreme degree in the case of alpha fiber, such fiber being more absorptive and cellular as a result of the extraction of appreciable quantities of impurities from the fiber. In the case of filled alpha fiber, the fiber cells are filled and the fiber coated so that the reacting fiber surface is diminished, the initial attack of the sulphuric acid is retarded, and the nitric acid is allowed to penetrate into the fibers in the proper concentration to form stable nitrates.

By lowering the reactivity of the cellulosic material, we also decrease the chance for local overheating in the nitrating acid bath. As is well known, an increase in the temperature at which nitration is conducted is generally followed by a decrease in yield of nitrocellu-

lose, particularly with wood cellulose, and, since nitration is a highly exothermic reaction, the chances for local overheating in the pulpy mixture of fibers and viscous nitrating acid are great unless steps are taken to retard the reaction so that the heat evolved may have opportunity to distribute itself uniformly throughout the entire mass.

The fiber may be filled while in either bulk or sheet form, and then nitrated in either form, but, inasmuch as nitration proceeds most favorably when the fiber is in the form of thin sheet or nitrating tissue, nitration is preferably performed on the fiber when in this condition.

The filling of the fiber while in sheet form may be carried out by various procedures, but each procedure aims to fill the fiber cells or voids and coat the fiber with nitrocellulose or regenerated cellulose. Thus, a thin water-leaf sheet made from alpha fiber may be treated by immersion in a relatively dilute solution of nitrocellulose in acetone or other solvent of, say, $\frac{1}{5}\%$ to $\frac{1}{4}\%$ concentration. The treatment may be carried out until the sheet has absorbed or retained the desired amount of nitrocellulose. The nitrocellulose filled sheet may then be dried and cut up into small squares or confetti, suitable for nitration.

Or cellulose may be regenerated in situ in the fiber cells and on the fiber by precipitation from a solution of suitable cellulose derivative. For example, a water-leaf sheet of alpha fiber may be passed through a solution of viscose of, say 1% cellulose concentration. The sheet may be completely dried or else partially dried, and then passed through a suitable setting bath, e. g. a solution of acetic acid or sodium bisulphate and sulphuric acid, thereby effecting a precipitation or regenerated cellulose in situ on the fiber and in the fiber cells. The sheet may then be washed substantially free of acid, steeped if desired in a sulphide-removing bath, e. g. a sulphite acid solution, again washed, dried, and cut up into squares or confetti suitable for nitration.

The filling of the fiber may be carried out while such fiber is in bulk or shredded condition. Thus, finely shredded alpha fiber may be uniformly treated with a solution of cellulose nitrate in acetone of, say, $\frac{1}{4}\%$ concentration. The fiber may then be nitrated in this condition.

Or the finely shredded fiber may be treated with a viscose solution of, say, 1% cellulose concentration. The excess solution may be expressed from the mass by centrifuging, whereupon the mass may be completely dried or else partially dried, then treated with a suitable setting solution. The fiber may then be washed substantially free of acid, steeped if desired in a sulphide-removing bath, again washed, dried, and finally nitrated.

Or the finely shredded fiber may be treated with a solution of nitrocellulose as in an alcohol-ether mixture, then denitrated by treatment with a strong solution of ammonium polysulphide for, say, one hour, at 80° F., washed, neutralized, again washed, thickened, dried, and finally nitrated. Sheeted fiber may be similarly treated. Cellulose may also be regenerated on sheeted or bulk fiber from a cuprammonium-cellulose solution.

Another procedure of filling fiber may be carried out similarly to the usual beater sizing process. In this case, a cellulose derivative, e. g., viscose, may be added to the alpha fiber in the beater engine, preferably after it has been beaten, and may then be uniformly disseminated throughout the fiber by the operation of the engine. Regenerated cellulose may then be precipitated on the fiber by the addition of a suitable precipitating agent, e. g., an acid mixture or acid salt, whereupon the fiber may be washed prior to sheeting. The fiber may then be sheeted into paper suitable for nitration.

Alpha fiber, filled as hereinbefore described, when nitrated, gives a higher yield of nitrocellulose and is accompanied by a lower acid retention than similar unfilled fiber. About 5% to 10% filling material may be incorporated into the fiber, but even 1% yields noteworthy improvement in nitrating characteristics. The nitrocellulose produced from the filled fiber is of high purity, and accordingly produces smooth, homogeneous and clear solutions in nitrocellulose solvents, from which better and stronger films and other products may be made than from solutions formed from nitrocellulose produced from similar unfilled fiber.

By the use of cellulose derivatives as nitrocellulose or regenerated cellulose as fillers, the decrease of absorptivity of the fiber is accomplished without the addition of material appearing as impurity in the final nitrated product.

Filling the fiber with regenerated cellulose or cellulose esters is also beneficial in the manufacture of esters other than the nitrate, leading to a higher yield of more uniform product.

Having thus explained the nature of this invention, it is evident that various changes in procedure might be resorted to without departing from its spirit or scope as defined by the appended claims.

We claim:

1. The step of conditioning cellulose fiber for conversion to cellulose derivatives, which comprises coating the fiber with a cellulose derivative.

2. The step of conditioning cellulose fiber for nitration, which comprises coating the fiber with nitrocellulose prior to nitration.

3. A process of conditioning cellulose fiber

for nitration, which comprises coating the fiber with a cellulose derivative and regenerating cellulose from the derivative.

4. A process of producing nitrocellulose from a high alpha cellulose wood fiber, which comprises coating the fiber with a cellulose derivative, and then nitrating the treated fiber.

5. A process of producing nitrocellulose from a high alpha cellulose wood fiber, which comprises treating the fiber with a solution of a cellulose derivative, regenerating cellulose from the derivative on the fiber, and then nitrating the fiber.

6. A process of producing nitrocellulose from a high alpha cellulose wood fiber, which comprises sheeting such fiber into a tissue, permeating the tissue with a cellulose derivative, and then nitrating the treated tissue.

7. A process of producing nitrocellulose from a high alpha cellulose wood fiber, which comprises sheeting such fiber into a tissue, permeating the tissue with a cellulose derivative, regenerating cellulose from the derivative, and nitrating the treated tissue.

8. A process of producing nitrocellulose from a high alpha cellulose wood fiber, which comprises sheeting such fiber into a tissue, permeating the tissue with nitrocellulose, and nitrating the treated tissue.

9. A process which comprises forming a

tissue of high alpha cellulose wood fiber permeated with regenerated cellulose, and nitrating the tissue.

10. A process which comprises forming a tissue of high alpha cellulose wood fiber permeated with a cellulose derivative regenerating cellulose from the derivative in situ in the tissue, and nitrating the tissue.

11. A nitratable tissue comprising high alpha cellulose wood fiber filled with regenerated cellulose.

12. A nitratable tissue comprising high alpha cellulose wood fiber permeated with a cellulose derivative.

13. A nitratable tissue comprising high alpha cellulose wood fiber permeated with nitrocellulose.

14. Material for nitration, comprising high alpha cellulose wood fiber coated with regenerated cellulose.

15. Material for nitration, comprising high alpha cellulose wood fiber coated with a cellulose derivative.

16. Material for nitration, comprising high alpha cellulose wood fiber coated with nitrocellulose.

In testimony whereof we have affixed our signatures.

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